

**CLAIMS**

What is claimed is:

5           1.     An electroplating bath for depositing a zinc-nickel ternary or higher alloy, comprising:

          a)     zinc ions;

          b)     nickel ions; and

          c)     one or more ionic species selected from ions of  $\text{Te}^{+4}$ ,  $\text{Bi}^{+3}$  and  $\text{Sb}^{+3}$ , with the proviso that when the ionic species comprises  $\text{Te}^{+4}$ , the bath  
10       further comprises one or more additional ionic species selected from ions of  $\text{Bi}^{+3}$ ,  $\text{Sb}^{+3}$ ,  $\text{Ag}^{+1}$ ,  $\text{Cd}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Cr}^{+3}$ ,  $\text{Cu}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{In}^{+3}$ ,  $\text{Mn}^{+2}$ ,  $\text{Mo}^{+6}$ ,  $\text{P}^{+3}$ ,  $\text{Sn}^{+2}$  and  $\text{W}^{+6}$ .

          2.     The bath of claim 1 wherein when the ionic species comprises one or more of  $\text{Bi}^{+3}$  or  $\text{Sb}^{+3}$ , the bath further comprises one or more additional ionic  
15       species selected from ions of  $\text{Ag}^{+1}$ ,  $\text{Cd}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Cr}^{+3}$ ,  $\text{Cu}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{In}^{+3}$ ,  $\text{Mn}^{+2}$ ,  $\text{Mo}^{+6}$ ,  $\text{P}^{+3}$ ,  $\text{Sn}^{+2}$  and  $\text{W}^{+6}$ .

          3.     The bath of claim 1 wherein the zinc ion and the nickel ion are present in the bath at concentrations sufficient to deposit a zinc-nickel alloy  
20       comprising a nickel content from about 3 wt% to about 25 wt% of the alloy.

          4.     The bath of claim 1 wherein the zinc ion and the nickel ion are present in the bath at concentrations sufficient to deposit a zinc-nickel alloy  
25       comprising a nickel content from about 8 wt% to about 22 wt% of the alloy.

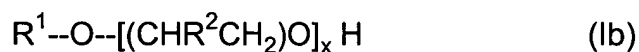
          5.     The bath of claim 1 further comprising one or more non-ionogenic, surface active polyoxyalkylene compound.

          6.     The bath of claim 5 wherein the one or more non-ionogenic surface  
30       active polyoxyalkylene compound comprises:

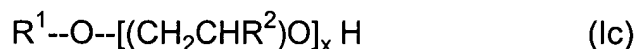
(i) one or more compound having a formula:



or

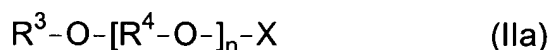


or



wherein  $R^1$  is an aryl or alkyl group containing up to about 24 carbon atoms,  $R^2$  is an alkyl group containing from 1 to about 4 carbon atoms,  $n$  is 2 or 3, and  $x$  is an integer between 2 and about 100;

(ii) one or more compound having a formula:



or



wherein  $R^3$  = a  $C_1$ - $C_{18}$  branched or unbranched alkyl, alkylene or alkynyl group, or phenyl- $O$ - $[R^5-O-]_m-CH_2-$ , in which  $m$  = 0-100 and  $R^5$  is a  $C_1$ - $C_4$  branched or unbranched alkylene;  $R^4$  =  $C_1$ - $C_4$  branched or unbranched alkylene;  $X$  = H,  $-SO_2Z$ ,  $-SO_3Z$ ,  $-SO_4Z$ ,  $-PO_3Z_2$ ,  $-PO_4Z_2$  (wherein  $Z$  independently may be H, an alkali metal ion, or  $Z_2$  may be an alkaline earth metal ion)  $-NH_2$ ,  $-Cl$  or  $-Br$ ;  $Y$  is an aliphatic polyhydroxy group, an amine group, a polyamine group or a mercaptan group, and  $a$  is equal to or less than the number of active hydrogens in OH,  $-NH$ ,  $NH_2$  or  $-SH$  groups on the  $Y$  component; or

(iii) a mixture of two or more of (i) and/or (ii).

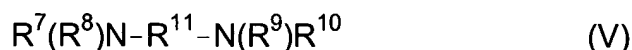
7. The bath of claim 1 wherein the bath comprises an acidic pH.

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8. The bath of claim 1 wherein the bath comprises an alkaline pH and further comprises a complexing agent.

5 9. The bath of claim 8 further comprising one or more non-ionogenic, surface active polyoxyalkylene compound.

10 10. The bath of claim 8 wherein the complexing agent comprises an aliphatic amine, a polymer of an aliphatic amine, a compound represented by the formula



15 wherein  $R^7$ ,  $R^8$ ,  $R^9$  and  $R^{10}$  are each independently alkyl or hydroxyalkyl groups provided that one or more of  $R^7$ - $R^{10}$  is a hydroxy alkyl group, and  $R^{11}$  is a hydrocarbylene group containing up to about 10 carbon atoms, or a mixture of two or more thereof.

20 11. A system for electroplating a substrate with a zinc-nickel ternary or higher alloy, comprising:

25 an electroplating apparatus including an electroplating cell for holding an electroplating bath, an anode, a cathode comprising the substrate to be electroplated, and a source of power operably connected to the anode and the cathode; and

an electroplating bath comprising:

- 25 a) zinc ions;  
b) nickel ions; and  
c) one or more ionic species selected from ions of  $Te^{+4}$ ,  $Bi^{+3}$  and  $Sb^{+3}$ , with the proviso that when the ionic species comprises  $Te^{+4}$ , the electroplating bath further comprises one or more additional ionic species

selected from ions of  $\text{Bi}^{+3}$ ,  $\text{Sb}^{+3}$ ,  $\text{Ag}^{+1}$ ,  $\text{Cd}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Cr}^{+3}$ ,  $\text{Cu}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{In}^{+3}$ ,  $\text{Mn}^{+2}$ ,  $\text{Mo}^{+6}$ ,  $\text{P}^{+3}$ ,  $\text{Sn}^{+2}$  and  $\text{W}^{+6}$ .

5           12.    The system of claim 11 wherein when the ionic species comprises one or more of  $\text{Bi}^{+3}$  or  $\text{Sb}^{+3}$ , the bath further comprises one or more additional ionic species selected from ions of  $\text{Ag}^{+1}$ ,  $\text{Cd}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Cr}^{+3}$ ,  $\text{Cu}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{In}^{+3}$ ,  $\text{Mn}^{+2}$ ,  $\text{Mo}^{+6}$ ,  $\text{P}^{+3}$ ,  $\text{Sn}^{+2}$  and  $\text{W}^{+6}$ .

10           13.    The system of claim 11 wherein the cell is separated into a cathodic chamber and an anodic chamber by a divider, and the electroplating bath is contained in the cathodic chamber.

15           14.    The system of claim 13 wherein the divider comprises one or more of a salt bridge, an ion-selective membrane, a sol-gel, an ion-selective anode coating, an anode-conforming ion-selective membrane and a porous ceramic.

20           15.    The system of claim 11 wherein the zinc ion and the nickel ion are present in the bath at concentrations sufficient to deposit a zinc-nickel alloy comprising a nickel content from about 3 wt% to about 25 wt% of the alloy.

            16.    The system of claim 11 wherein the zinc ion and the nickel ion are present in the bath at concentrations sufficient to deposit a zinc-nickel alloy comprising a nickel content from about 8 wt% to about 22 wt% of the alloy.

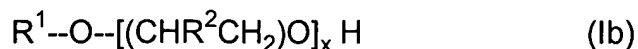
25           17.    The system of claim 11 wherein the bath further comprises one or more non-ionogenic, surface active polyoxyalkylene compound.

            18.    The system of claim 17 wherein the one or more non-ionogenic surface active polyoxyalkylene compound comprises:

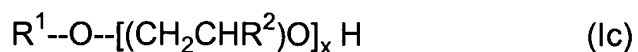
30           (i) one or more compound having a formula:



or

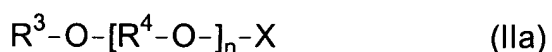


or



wherein  $R^1$  is an aryl or alkyl group containing up to about 24 carbon atoms,  $R^2$  is an alkyl group containing from 1 to about 4 carbon atoms,  $n$  is 2 or 3, and  $x$  is an integer between 2 and about 100;

(ii) one or more compound having a formula:



or



wherein  $R^3$  = a  $C_1$ - $C_{18}$  branched or unbranched alkyl, alkylene or alkynyl group, or phenyl- $O$ - $[R^5-O]_m-CH_2-$ , in which  $m$  = 0-100 and  $R^5$  is a  $C_1$ - $C_4$  branched or unbranched alkylene;  $R^4$  =  $C_1$ - $C_4$  branched or unbranched alkylene;  $X$  = H,  $-SO_2Z$ ,  $-SO_3Z$ ,  $-SO_4Z$ ,  $-PO_3Z_2$ ,  $-PO_4Z_2$  (wherein  $Z$  independently may be H, an alkali metal ion, or  $Z_2$  may be an alkaline earth metal ion)  $-NH_2$ ,  $-Cl$  or  $-Br$ ;  $Y$  is an aliphatic polyhydroxy group, an amine group, a polyamine group or a mercaptan group, and  $a$  is equal to or less than the number of active hydrogens in OH,  $-NH$ ,  $NH_2$  or  $-SH$  groups on the  $Y$  component; or

(iii) a mixture of two or more of (i) and/or (ii).

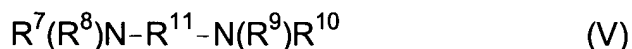
19. The system of claim 11 wherein the bath comprises an acidic pH.

20. The system of claim 11 wherein the bath comprises an alkaline pH and further comprises a complexing agent.

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21. The system of claim 20 wherein the bath further comprises one or more non-ionogenic, surface active polyoxyalkylene compound.

22. The system of claim 20 wherein the complexing agent comprises an aliphatic amine, a polymer of an aliphatic amine, a compound represented by the formula



wherein  $R^7$ ,  $R^8$ ,  $R^9$  and  $R^{10}$  are each independently alkyl or hydroxyalkyl groups provided that one or more of  $R^7$ - $R^{10}$  is a hydroxy alkyl group, and  $R^{11}$  is a hydrocarbylene group containing up to about 10 carbon atoms, or a mixture of two or more thereof.

23. A system for electroplating a substrate with a zinc-nickel ternary or higher alloy, comprising:

an electroplating apparatus including an electroplating cell for holding an electroplating bath, the chamber having a divider separating the cell into a cathodic chamber and an anodic chamber, an anode in the anodic chamber, a cathode in the cathodic chamber, the cathode comprising the substrate to be electroplated, and a source of power operably connected to the anode and the cathode; and

an electroplating bath in the cathodic chamber comprising:

- a) zinc ions;
- b) nickel ions; and
- c) one or more ionic species selected from ions of  $Te^{+4}$ ,  $Bi^{+3}$  and  $Sb^{+3}$ .

24. The system of claim 23 wherein the bath further comprises one or more additional ionic species selected from ions of  $\text{Ag}^{+1}$ ,  $\text{Cd}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Cr}^{+3}$ ,  $\text{Cu}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{In}^{+3}$ ,  $\text{Mn}^{+2}$ ,  $\text{Mo}^{+6}$ ,  $\text{P}^{+3}$ ,  $\text{Sn}^{+2}$  and  $\text{W}^{+6}$ .

25. The system of claim 23 wherein the zinc ion and the nickel ion are present in the bath at concentrations sufficient to deposit a zinc-nickel alloy comprising a nickel content from about 3 wt% to about 25 wt% of the alloy.

26. The system of claim 23 wherein the zinc ion and the nickel ion are present in the bath at concentrations sufficient to deposit a zinc-nickel alloy comprising a nickel content from about 8 wt% to about 22 wt% of the alloy.

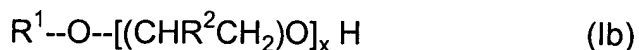
27. The system of claim 23 wherein the bath further comprises one or more non-ionogenic, surface active polyoxyalkylene compound.

28. The system of claim 27 wherein the one or more non-ionogenic surface active polyoxyalkylene compound comprises:

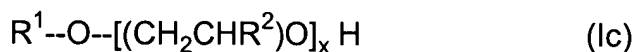
(i) one or more compound having a formula:



or

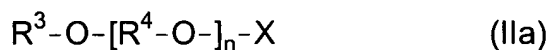


or



wherein R<sup>1</sup> is an aryl or alkyl group containing up to about 24 carbon atoms, R<sup>2</sup> is an alkyl group containing from 1 to about 4 carbon atoms, n is 2 or 3, and x is an integer between 2 and about 100;

(ii) one or more compound having a formula:



or



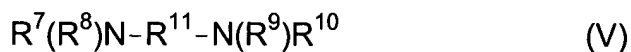
- 5 wherein  $R^3$  = a  $C_1$ - $C_{18}$  branched or unbranched alkyl, alkylene or alkynyl group, or phenyl- $O-[R^5-O]_m-CH_2-$ , in which  $m = 0$ -100 and  $R^5$  is a  $C_1$ - $C_4$  branched or unbranched alkylene;  $R^4$  =  $C_1$ - $C_4$  branched or unbranched alkylene;  $X = H$ ,  $-SO_2Z$ ,  $-SO_3Z$ ,  $-SO_4Z$ ,  $-PO_3Z_2$ ,  $-PO_4Z_2$  (wherein  $Z$  independently may be  $H$ , an alkali metal ion, or  $Z_2$  may be an alkaline earth metal ion)  $-NH_2$ ,  $-Cl$  or  $-Br$ ;  $Y$  is
- 10 an aliphatic polyhydroxy group, an amine group, a polyamine group or a mercaptan group, and  $a$  is equal to or less than the number of active hydrogens in  $OH$ ,  $-NH$ ,  $NH_2$  or  $-SH$  groups on the  $Y$  component; or
- (iii) a mixture of two or more of (i) and/or (ii).

15 29. The system of claim 23 wherein the bath comprises an acidic pH.

30. The system of claim 23 wherein the bath comprises an alkaline pH and further comprises a complexing agent.

20 31. The system of claim 30 wherein the bath further comprises one or more non-ionogenic, surface active polyoxyalkylene compound.

25 32. The system of claim 30 wherein the complexing agent comprises an aliphatic amine, a polymer of an aliphatic amine, a compound represented by the formula



30 wherein  $R^7$ ,  $R^8$ ,  $R^9$  and  $R^{10}$  are each independently alkyl or hydroxyalkyl groups provided that one or more of  $R^7$ - $R^{10}$  is a hydroxy alkyl group, and  $R^{11}$  is a



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hydrocarbylene group containing up to about 10 carbon atoms, or a mixture of two or more thereof.

5           33.    The system of claim 23 wherein the divider comprises one or more of a salt bridge, an ion-selective membrane, a sol-gel, an ion-selective anode coating, an anode-conforming ion-selective membrane and a porous ceramic.

          34.    An article comprising a zinc-nickel ternary or higher alloy, the alloy comprising:

10           zinc;

          nickel; and

          one or more element selected from Te, Bi, and Sb, with the proviso that when the alloy comprises Te, the alloy further comprises one or more additional element selected from Bi, Sb, Ag, Cd, Co, Cr, Cu, Fe, In, Mn, Mo, P, Sn and W.

15           35.    The article of claim 34 wherein the alloy is a higher alloy comprising one or more of Bi and Sb, and further comprises one or more additional element selected from Ag, Cd, Co, Cr, Cu, Fe, In, Mn, Mo, P, Sn and W.

20           36.    An article comprising a zinc-nickel quaternary or higher alloy, the alloy comprising:

          zinc;

          nickel;

          one or more element selected from Te, Bi and Sb; and

25           one or more element selected from Ag, Cd, Co, Cr, Cu, Fe, In, Mn, Mo, P, Sn and W.

          37.    A process for forming a zinc-nickel ternary or higher alloy, comprising:

30           immersing a substrate in the bath of claim 1; and

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carrying out an electroplating process with the bath to deposit on the substrate the alloy comprising one or more element corresponding to the one or more ionic species.

5                    38.    A process for forming a zinc-nickel ternary or higher alloy, comprising:

immersing a substrate in the bath of claim 2; and

10                   carrying out an electroplating process with the bath to deposit on the substrate the alloy comprising one or more element corresponding to the one or more ionic species.

39.    A process for forming a zinc-nickel ternary or higher alloy, comprising:

immersing a substrate in the bath of claim 11; and

15                   operating the electroplating apparatus to deposit on the substrate the alloy comprising one or more element corresponding to the one or more ionic species.

40.    A process for forming a zinc-nickel ternary or higher alloy, comprising:

20                   immersing a substrate in the bath of claim 12; and

operating the electroplating apparatus to deposit on the substrate the alloy comprising one or more element corresponding to the one or more ionic species.

41.    A process for forming a zinc-nickel ternary or higher alloy, comprising:

25                   immersing a substrate in the bath of claim 23; and

operating the electroplating apparatus to deposit on the substrate the alloy comprising one or more element corresponding to the one or more ionic species.

42. A process for forming a zinc-nickel ternary or higher alloy,  
comprising:  
immersing a substrate in the bath of claim 24; and  
operating the electroplating apparatus to deposit on the substrate the alloy  
comprising one or more element corresponding to the one or more ionic species.

43. An electroplating bath for depositing a zinc-nickel ternary or higher  
alloy, comprising:

- a) zinc ions;
- b) nickel ions; and
- c) one or more ionic species selected from ions of  $\text{Te}^{+4}$ ,  $\text{Bi}^{+3}$  and  $\text{Sb}^{+3}$ , with the proviso that when the ionic species comprises  $\text{Te}^{+4}$ , the bath is free of a mixture of brighteners comprising both (i) reaction product of epihalohydrin with alkylene amines such as ethylenediamine or its methyl-substituted derivatives; propylenediamine or its methyl-substituted derivatives; diethylenetriamine or its methyl-substituted derivatives; and higher alkylene polyamines, and (ii) aromatic aldehydes.

44. The bath of claim 43 wherein the bath further comprises one or more additional ionic species selected from ions of  $\text{Ag}^{+1}$ ,  $\text{Cd}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Cr}^{+3}$ ,  $\text{Cu}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{In}^{+3}$ ,  $\text{Mn}^{+2}$ ,  $\text{Mo}^{+6}$ ,  $\text{P}^{+3}$ ,  $\text{Sn}^{+2}$  and  $\text{W}^{+6}$ .